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Fano resonance of LO-phonon-coupled excited states of Li acceptors in ZnSe and Luttinger parameters

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Fano resonance between LO-phonon-coupled excited states of a Li acceptor and the valence-band state has been observed in bulk ZnSe through the infrared-absorption measurements. For the $2P_{5/2}(\Gamma_7)$ state of a Li acceptor, we found that the coupling strength of the Fano resonance $f(h\nu_0)$ is 2.8 cm^{-1}, the distortion parameter q is 1.07, and the spectral width of the coupled state Γ is 16.8 cm^{-1}. It is concluded that a significant feature of the resonance peak is due to strong hole LO-phonon coupling in ZnSe. The Luttinger parameters γ_1, γ_2, and γ_3 are estimated to be 6.44, 2.58, and 2.74, respectively. [S0163-1829(99)12443-3]

Mixing of a state with the others is one of the most intriguing appearances of quantum mechanics. A distorted peak in the inelastic-scattering cross section of electrons with He atom was analyzed by Fano as the interference of a discrete state with a continuum.[1] The so-called Fano resonance has been reported in the optical spectra of semiconductors. For example, absorption spectra of excitons in Cu_2O reveal distorted line shape and have been explained by interference between the discrete state of direct excitons and the continuum state of indirect excitons.[2] Furthermore, Fano resonances have been observed in spectra of deep impurities in Ge, Si, and GaAs.[3–5] In particular, Piao *et al.* proposed a conventional method to estimate the characteristic parameters of the resonance.[3] After their method, we estimate the parameters related to resonances observed in our experiment.

Recently, we have observed infrared absorption of Li acceptors in addition to shallow donors, Cl, Al, and In in ZnSe.[6] Only one absorption peak among more than ten peaks was definitely assigned to the $1S$–$2P$ transition of a Li acceptor, as reported in our previous paper.[6] In comparison with photoluminescence experiment and theoretical work, most of the peaks below the ionization energy of Li acceptors have been ascribed to the optical transition from the $1S$ ground state to the excited states of a Li acceptor.[7] The peaks observed in the energy range above the ionization energy of a Li acceptor are broad and distorted. We assign the peaks to Fano resonances between the LO-phonon-coupled excited states of a Li acceptor and the valence-band states. We found that energy separation between the peaks due to the fundamental transition and the corresponding Fano resonance is almost the same as the energy of LO phonon at a Γ point.

The structure of the valence band in ZnSe has been so far studied by magnetoreflectance, cyclotron resonance, and photoluminescence excitation measurements.[8–10] The values of the Luttinger parameters γ_1, γ_2, and γ_3, which characterize the figure of the valence band, have not been precisely determined until now. In particular, the anisotropy parameter $\delta=(\gamma_3-\gamma_2)/\gamma_1$ is controversial, i.e., Venghaus reported the considerable anisotropy $\delta=0.17$, while Ohyama *et al.* observed isotropic mass of the heavy hole through the angle dependence of cyclotron resonance.[9] In this work, we determine the Luttinger parameters and predict the mass of the light hole.

The samples we used in this study were bulk ZnSe grown by solid growth method. The typical size of the sample is $4\times4\times1\ \mathrm{mm}^3$. The sample was placed on the cold finger attached to the liquid-He container. A Fourier-transformed infrared spectrometer (Analect; AQS20) with a $Hg_xCd_{1-x}Te$ detector was employed to measure the infrared-absorption spectra. The resolution of the instrument was about 2 cm^{-1}, and the low resolution hinders the interference of reflection between the front and back surfaces of the sample.

Figure 1 shows infrared absorption of ZnSe at two different temperatures. The absorption peaks should be related to impurities because the peak intensity decreases with increasing temperature. Invariance of the peak profile in regard to the exchange of samples suggests that those samples contain only one species of impurity. Baldereschi and Lipari calculated the energy of a hole bound to an acceptor in a cubic crystal.[11] According to their notation, the lowest energy peak is assigned to the $1S_{3/2}$–$2P_{3/2}$ transition of a hole bound to Li acceptor as reported in the previous paper, where the suffix denotes the total angular momentum $\boldsymbol{F}$, which is the summation of the total angular momentum of a free hole $\boldsymbol{J}$ and the orbital angular momentum of hydrogenlike motion $\boldsymbol{L}$.[6]

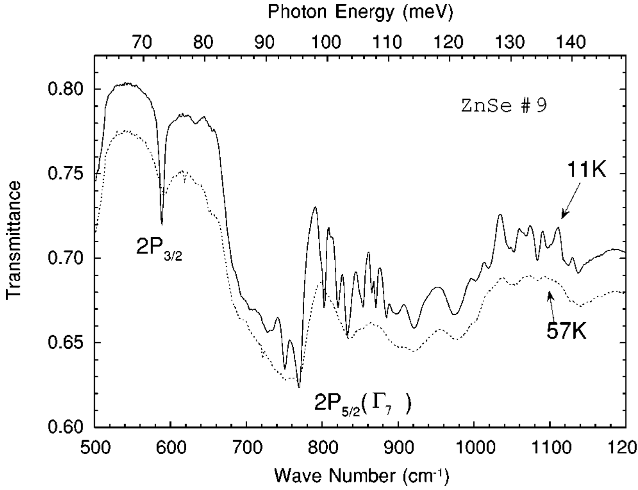

FIG. 1. Infrared absorption of bulk ZnSe at two different temperatures. Absorption intensities increase with decreasing temperature. Absorption peaks are denoted by the final states of transitions.

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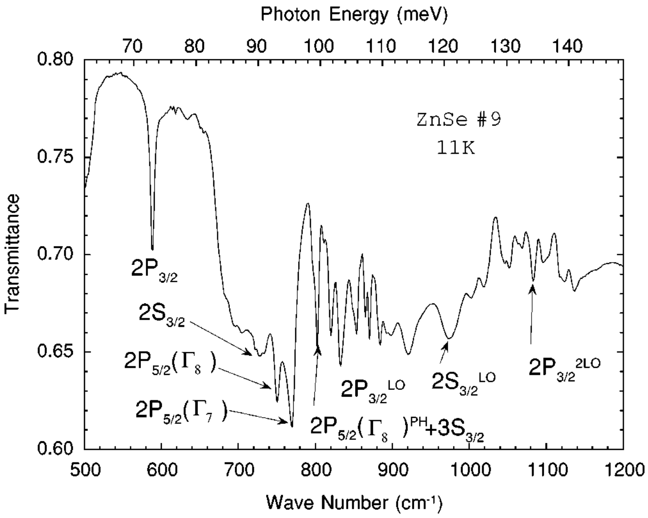

FIG. 2. Infrared absorption of Li acceptors in a ZnSe sample and the peak assignment.

Tew *et al.* observed photoluminescence excitation spectra of different donor-acceptor pair emission bands and selective luminescence in ZnSe and estimated energy separation between the ground state and the excited state of Li and Na acceptors. Referring to their results, we assigned the observed peaks in our experiment to the transition of a hole bound to a Li acceptor as shown in Fig. 2. The absorption peak at the lowest energy is due to the $1S_{3/2}$–$2P_{3/2}$ transition of a hole bound to a Li acceptor as reported in our previous paper.[6] The excited state of $2P_{5/2}$ is split into two levels, $2P_{5/2}(\Gamma_8)$ and $2P_{5/2}(\Gamma_7)$, by a crystal field with cubic symmetry. They are more intensive than in the case of acceptors in Ge.[13] We assume that the strong twin peaks around 90 meV are due to $1S_{3/2}-2P_{5/2}(\Gamma_8)$ and $1S_{3/2}-2P_{5/2}(\Gamma_7)$.

We estimate the Luttinger parameters γ_1, γ_2, and γ_3 from the peak positions of the $2P_{5/2}$ twin peaks and the cyclotron mass $1.04m_0$ of the heavy hole in the direction of [111] observed by Ohyama *et al.*[9] We did not refer to the peak position of $1S_{3/2}-2P_{3/2}$ because the $2P_{3/2}$ state is somewhat suffered from central-cell correction due to finite probability on the impurity core.[11] The obtained values of Luttinger parameters γ_1, γ_2, and γ_3 are 6.44, 2.58, and 2.74, respectively, and the effective Rydberg R_0 is estimated to be 30.5 meV. We used $\epsilon_s = 8.33$ as the static dielectric constant in ZnSe. We could derive the ionization energy 2.9 meV of the $2P_{1/2}$ state from the table by Baldereschi and Lipari by using the Luttinger parameters and the effective Rydberg.[12] The ionization energies of $2P_{5/2}(\Gamma_8)$ and $2P_{1/2}$ provide us with an energy difference between the $1S_{3/2}-2P_{5/2}(\Gamma_8)$ and $1S_{3/2}-2P_{1/2}$ peaks. In this way, we assigned a peak at 107.3 meV to the $1S_{3/2}-2P_{1/2}$ as shown in Fig. 3. As a result, we could estimate the ionization energy of the $1S_{3/2}$ ground state to be 110.2 meV.

Furthermore, several peaks have been observed at the energy region above the ionization energy of a Li acceptor as depicted in Fig. 4. Their broad and distorted line shapes are peculiar to Fano resonance and the peaks above the ionization energy are replicas of fundamental ones observed below it. Energy difference between the original peak and the replica is about 32 meV, which is nearly equal to the energy of LO phonon at Γ point. As a result, the peaks above the ionization energy of a Li acceptor correspond to Fano resonance, i.e., the transition to interference states between LO-phonon-coupled excited states of a Li acceptor and the valence band. We assign the peaks at 124.5 and 126.4 meV to $1S_{3/2}-2P_{5/2}(\Gamma_8)^{\mathrm{LO}}$ and $1S_{3/2}-2P_{5/2}(\Gamma_7)^{\mathrm{LO}}$, respectively. The superscript LO denotes the LO-phonon-coupled state.

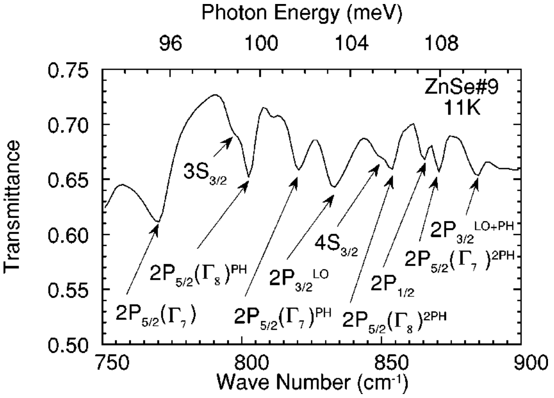

FIG. 3. Infrared-absorption spectrum at the wave-number range of 750–900 cm^{-1}.

According to Piao *et al.*, the line shape of Fano resonance is calculated by the Fano ratio:

$$F(\epsilon,q)=\frac{(q+\epsilon)^2}{1+\epsilon^2}. \tag{1}$$

Here q is a dimensionless parameter that characterizes the admixture of the valence-band state and the compound state, i.e., the LO-phonon-coupled excited state. The dimensionless variable ϵ is defined by

$$\epsilon=\frac{h\nu-[E_{bh}+h\nu_{\mathrm{opt}}+f(h\nu)]}{\frac{1}{2}\Gamma}. \tag{2}$$

Here, $h\nu$ and $h\nu_{\mathrm{opt}}$ are the energies of incident photons and optical phonons, respectively, and E_{bh} is the energy of the bound hole. $f(h\nu)$ is a measure of the strength of the coupling between the compound state and the resonance valence-band state. Γ is the spectral width of the compound state. For the resonance $2P_{5/2}(\Gamma_7)^{\mathrm{LO}}$, we estimate the parameters $f(h\nu_0)$, q, and Γ, where $f(h\nu_0)$ means the value of $f(h\nu)$ at $\epsilon=0$. $f(h\nu_0)$, q, and Γ are 2.8 cm^{-1}, 1.07, and

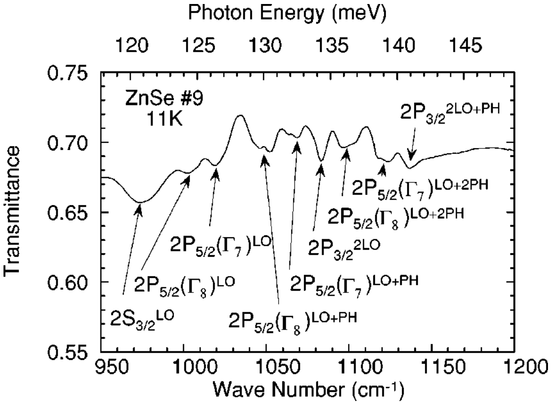

FIG. 4. Fano resonance between the LO-phonon-coupled excited state of acceptor and the valence band.

16.8 cm^{-1}, respectively. We found that $f(h\nu_0)$ is almost twice as large as the case of Zn^- in Ge.

An above-mentioned fact signifies that the coupling is rather strong as the compound states exist near the edge of the valence band. In fact, the ratio in the peak intensity of the Fano resonance to the fundamental absorption increases as the photon energy approaches the ionization energy of the impurity. The intensity of the Fano resonance in ZnSe:Li is much stronger than that in Ge:Zn^- as expected from the magnitude of $f(h\nu_0)$.

In Fig. 4 we notice a relatively stronger line around 120 meV. We speculate that the peak is due to the Fano resonance of $1S_{1/2}-2S_{3/2}^{\mathrm{LO}}$ because the extension of the *S*-like wave function in the momentum space leads to strong coupling between the discrete level and the continuum. As a result, it is concluded that the peak at 90.31 meV is caused by the transition of $1S_{3/2}-2S_{3/2}$. In addition, the LO-phonon replica of the $1S_{3/2}-2P_{3/2}$ peak is observed around 103 meV, and the two-phonon replica appears around 134 meV. Twin peaks around 100 meV are assigned to the phonon replica of $1S_{3/2}-2P_{5/2}(\Gamma_8)$ and $1S_{3/2}-2P_{5/2}(\Gamma_7)$ peaks. The energy of associated phonon is 6.27 meV. This phonon may be a localized one. Moreover, the two-phonon replica denoted as 2PH and their Fano resonances have been observed. The Fano resonances $2P_{5/2}(\Gamma_8)^{\mathrm{PH+LO}}$ and $2P_{5/2}(\Gamma_7)^{\mathrm{PH+LO}}$ reveal fine doublet structures, which might originate in the difference in intermediate state.

The ionization energies of *nS* states can be estimated from the empirical equation $E_{ns}=E_A n^{-1.76}$ introduced by Cohen and Sturge.[14] We calculated the ionization energies by this equation with the ionization energy of the $2S_{3/2}$ state to be 19.9 meV with the above equation. The energies of the $3S_{3/2}$ and $4S_{3/2}$ states are 9.8 and 5.9 meV, respectively. Accordingly, the corresponding transition energies of $1S_{3/2}-3S_{3/2}$ and $1S_{3/2}-4S_{3/2}$ become 100.4 and 104.3 meV, respectively. Both absorption peaks overlap with $2P_{5/2}(\Gamma_8)^{\mathrm{PH}}$ and $2P_{5/2}(\Gamma_8)^{\mathrm{2PH}}$, respectively.

Tew *et al.* compared their experimental results with calculated results with Luttinger parameters obtained by Venghaus.[7,8] Their experimental results agree well with the calculated ones. However, they overestimated the anisotropy parameter δ because of their different peak assignment. Ohyama *et al.*, on the other hand, reported no anisotropy of heavy-hole mass.[9] We estimated the anisotropy of heavy-hole mass by using the obtained parameters, and it was found that the heavy-hole mass along the [111] direction is $1.04m_0$ and that along the [110] direction is $0.96m_0$. The difference is only 8% and is within the experimental error because of broad linewidth of cyclotron resonance. The mass of the light hole in ZnSe is estimated to be $0.085m_0$, and further experimental investigation is required to confirm the value.

In conclusion, we observed infrared absorption due to the hole transition of a Li acceptor. The absorption peaks are assigned by referring to the previous experimental and theoretical works. Fano resonances between LO-phonon-coupled excited states of the acceptor and the valence-band state have been observed in bulk ZnSe. The Luttinger parameters γ_1, γ_2, and γ_3 are estimated to be 6.44, 2.58, and 2.74, respectively. The small anisotropy anticipated from those parameters is in good agreement with cyclotron resonance experiment.

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